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Chemical Stability of the Fiber Coating/Matrix Interface in Silicon-Based Ceramic Matrix Composites

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Carbon and boron nitride are used as fiber coatings in silicon-based composites. In order to assess the long-term stability of these materials, reactions of carbon/Si_3N_4 and BN/SiC were studied at high temperatures with Knudsen effusion, coupon tests, and by microstructural examination. In the carbon/Si_3N_4 system, carbon reacted with Si_3N_4 to form gaseous N_2 and SiC. The formation of SiC limited further reaction by physically separating the carbon and Si_3N_4. Consequently, the development of high $p(N_2)$ at the interface, predicted from thermochemical calculations, did not occur, thus limiting the potential deleterious effects of the reaction on the composite. Strong indications of a reaction between BN and SiC were shown by TEM and SIMS analysis of the BN/SiC interface. In long-term exposures, this reaction can lead to a depletion of a BN coating and/or an unfavorable change of the interfacial properties, limiting the beneficial effects of the coating.

I. Introduction

FIBER-REINFORCED ceramic composites are an emerging class of high-temperature structural materials. This is primarily due to their potential for enhanced mechanical properties, such as fracture toughness and strength, and the resultant increased reliability as structural components. However, one of the key areas to be critically addressed for the realization of the full potentials of composites is the fiber/matrix interface. The interface must be chemically stable. In addition, in systems where the matrix is brittle, the fiber/matrix interface bonding has to be optimized to promote the load transfer from the matrix to the fibers and to permit the matrix microcrack deflection.[1] One approach to optimize interfacial properties is to apply fiber coatings.

Some of the most promising composites for high-temperature structural applications are SiC fiber/Si_3N_4 matrix and SiC fiber/SiC matrix systems. To limit fiber/matrix bonding, the fibers are coated with carbon or boron nitride (BN). In the event of matrix cracking, these coatings will readily oxidize; however, this issue is beyond the scope of this paper and has been treated in detail elsewhere.[2–4]

Ideally, the matrix will not crack and the interface will remain at a low oxygen potential for long times. The purpose of this paper is to investigate the chemical stability of the interface coating in SiC fiber/SiC matrix and SiC fiber/Si_3N_4 matrix systems and its implication on the long-term durability of these composites.

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II. Thermodynamic Considerations

(1) *Carbon/Si_3N_4 System*

Carbon can react with Si_3N_4 according to reaction (1), producing $N_2(g)$ and SiC(s).

$$Si_3N_4 + 3C = 3SiC + 2N_2(g) \quad (1)$$

Some $N_2(g)$ can also be generated by the vaporization of Si_3N_4.

$$Si_3N_4 = 3Si + 2N_2(g) \quad (2)$$

The SOLGASMIX-PV program[5] in conjunction with JANAF thermochemical data[6] was used to calculate $p(N_2)_{eq}$ for reactions (1) and (2) as shown in Fig. 1. Note that $p(N_2)_{eq}$ is independent of the Si_3N_4/C ratio, although the calculation was carried out for a 1:1 mixture. The reaction between carbon and Si_3N_4 substantially increased $p(N_2)_{eq}$ when compared to $p(N_2)_{eq}$ in pure Si_3N_4. The formation of nitrogen gas at pressures near 10^5 Pa within the composite may cause some internal damage. If nitrogen has a route for escape, such as a microcrack or pore, the carbon coating will be depleted.

(2) *BN/SiC System*

The potential reactions between BN and SiC include

$$SiC + 4BN = B_4C + Si(g) + 2N_2(g) \quad (3a)$$

$$3SiC + 12BN = Si_3N_4 + 3B_4C(s) + 4N_2(g) \quad (3b)$$

$$C \text{ (excess C in SiC)} + 4BN(s) = B_4C + 2N_2(g) \quad (3c)$$

Some $N_2(g)$ and Si(g) can be generated by the vaporization of BN and SiC, respectively.

$$BN = B + \tfrac{1}{2}N_2(g) \quad (4a)$$

$$SiC = Si(g) + C \quad (4b)$$

Figure 2 compares $p(N_2)_{eq} + p(Si)_{eq}$ in the reacted SiC/BN

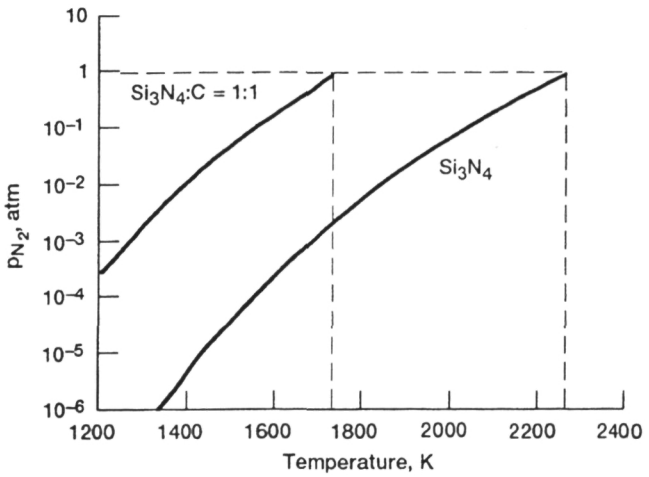

Fig. 1. Calculated pressure of $N_2(g)$ for Si_3N_4 and the carbon/Si_3N_4 system.

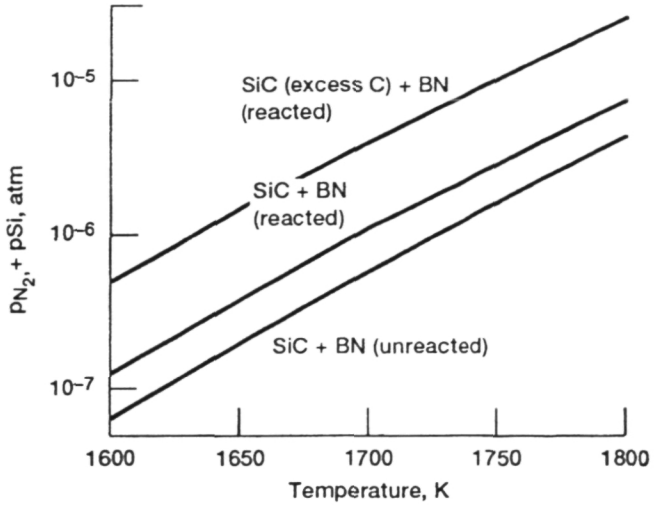

Fig. 2. Calculated pressure of $N_2(g)$ + $Si(g)$ for the reacted and unreacted BN/SiC system.

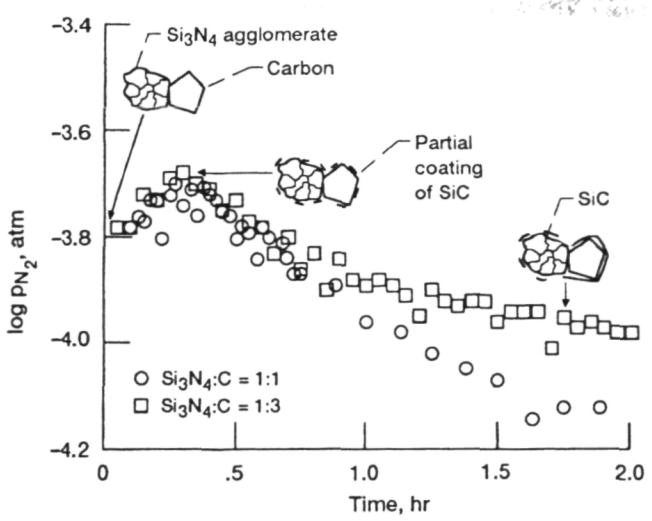

Fig. 4. Pressure of $N_2(g)$ for the carbon/Si_3N_4 system at 1600 K determined by the Knudsen effusion test.

system with that in the unreacted SiC/BN system. The reaction of BN with SiC or excess carbon in SiC slightly increased the total gaseous pressure, indicating that limited reactions between BN and SiC occur. However, the pressure is so low that the reaction is not likely to cause any mechanical instability to the SiC fiber/SiC matrix composites utilizing BN fiber coating. Nevertheless, the BN coating can be depleted if escape routes for N_2 form. Another potential reaction is the formation of a BN-C solid solution, $(BN)_xC_{1-x}$.[7,8] With a carbon-rich SiC matrix, this may lead to eventual diffusion of the BN coating into the substrate.

III. Experimental Procedure

Knudsen effusion and coupon tests were employed in this study to investigate the reactions at the carbon/Si_3N_4 and BN/SiC interfaces. Knudsen effusion was done with powders to obtain information on the gaseous and solid products. Coupon studies provided further information on the solid products.

(1) Knudsen Effusion Test

Knudsen effusion is a classic technique for the study of equilibrium between condensed and gaseous phases.[9] Intimately mixed powders of reactants are placed in the Knudsen cell with a small orifice and heated up to a reaction temperature in a vacuum. If the orifice is sufficiently small, equilibrium is established inside the cell. The effusion rate of gaseous reaction products through the orifice is measured with a microbalance, as shown in Fig. 3. The resolution of the microbalance/Knudsen cell system is ±0.001 mg. From the effusion rate, the total vapor pressure is calculated using the Hertz–Knudsen–Langmüir equation.[9]

$$P = (dw/dt)(1/A)(2\pi RT/M)^{1/2}$$
$$= 6.27 \times 10^{-6}\,(dw/dt)(1/A)(T/M)^{1/2} \quad (5)$$

Here P is vapor pressure in atm, dW/dt is mass effusion rate in g/h, A is orifice area in cm^2, T is absolute temperature, R is the gas constant, and M is the weighted average molecular weight of the vapor species. Details of the experimental setup are described elsewhere.[10] Previous work has demonstrated that the Knudsen effusion technique can be applied to a detailed study of interfacial reactions.[10]

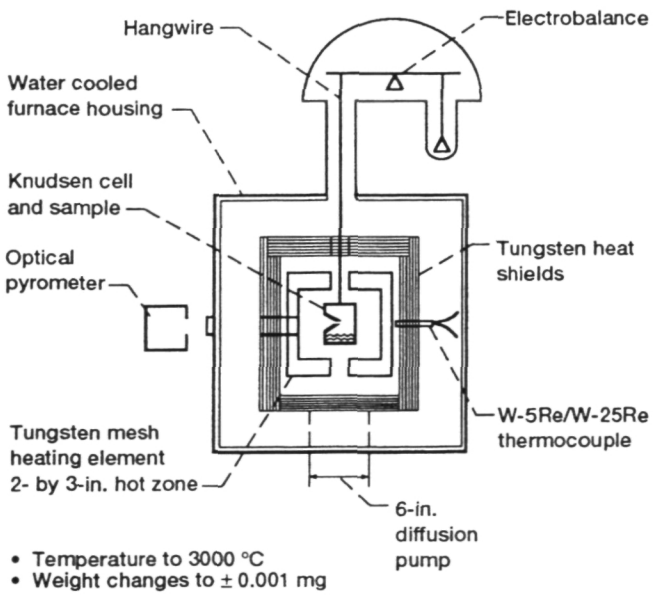

Fig. 3. Schematic of vacuum thermogravimetric apparatus in conjunction with a Knudsen cell.

It is critical that Knudsen cell materials be inert to both the reactants and the products. We found that graphite and molybdenum were adequate for carbon/Si_3N_4 reaction and BN/SiC reaction, respectively. It appears that the molybdenum cell forms a protective inner coating of $MoSi_2$ which is inert to the BN/SiC mixture. Therefore, prior to the investigation of the BN/SiC reaction, preliminary runs to form $MoSi_2$ coating inside the molybdenum cell were carried out. High-purity powders of carbon, Si_3N_4, BN, and SiC were used as the reactants. Powder particle diameters varied from 1 to 100 μm for carbon and 10 to 150 μm for Si_3N_4, SiC, and BN, which were agglomerates of finer particles with 0.1–1 μm diameter. After testing, powders were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS).

(2) Coupon Test

Coated coupons were employed to closely simulate the condition at the fiber/matrix interface and provide additional information on any solid products formed. Chemically vapor-deposited (CVD) Si_3N_4 and SiC coupons (1 cm × 1 cm × 0.2 cm) were polished to 1 μm with diamond paste, and any residual surface SiO_2 was dissolved in 10% HF. Carbon (0.1 μm thick) and BN (0.3 μm thick) were deposited on the polished surface of Si_3N_4 and SiC using a spark coater and CVD, respectively. After the coated coupons were heat treated under vacuum (6.7×10^{-5} Pa) at high temperatures (1650 K for C/Si_3N_4 and 1730 K for BN/SiC), the coating/substrate interface was analyzed with TEM and secondary ion mass spectrometry (SIMS).

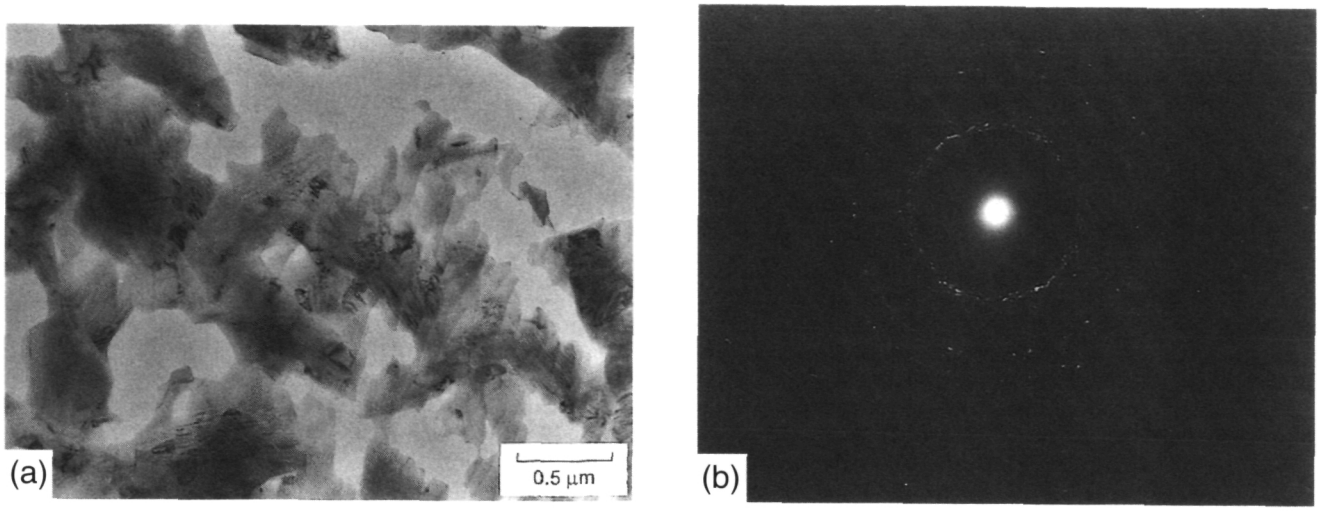

Fig. 5. TEM analysis of the carbon/Si_3N_4 interface for a carbon-coated Si_3N_4 coupon after 45 h under vacuum at 1650 K. (a) TEM image. (b) Electron diffraction pattern.

IV. Results and Discussion

(1) Carbon/Si_3N_4 System

Figure 4 shows $p(N_2)$ for the Si_3N_4/C reaction determined from Knudsen effusion tests at 1600 K. The $p(N_2)$ initially increased until it reached the maximum pressure after about 15 min. It remained constant for about 10–15 min and then decreased gradually. Mixtures with a lower C/Si_3N_4 ratio exhibited a more rapid decrease of $p(N_2)$. EDS showed a high silicon concentration on carbon particles after 2 h, which was due to the SiC formed by reaction (1) as was identified by XRD. The EDS silicon peak was significant by 30 min, although XRD did not show SiC peaks until later. It appears that SiC already formed by 30 min, but its amount was below the resolution of XRD. The formation of SiC on carbon particles as early as 30 min and the gradual decrease of $p(N_2)$ after the maximum at 15–30 min indicate that SiC caused the gradual decrease of $p(N_2)$ by separating the carbon and the Si_3N_4, thus acting as a physical reaction barrier.

Coupon tests also confirmed the formation of SiC at the C/Si_3N_4 interface. After a heat treatment in 6.7×10^{-7} Pa at 1650 K for 45 h, the coating on the Si_3N_4 coupon was completely delaminated. The delamination presumably occurred during the cooling, due to the coefficient of thermal expansion (CTE) mismatch at the interface. The TEM image and electron diffraction pattern of the interface are shown in Fig. 5. The electron diffraction ring pattern matches that of β-SiC, confirming the formation of a polycrystalline β-SiC.

In a recent study employing fiber push-out and fracture tests, in conjunction with Auger electron spectrometry (AES) depth profiles, SiC was not detected at the interface of a carbon-coated SiC fiber/reaction-bonded Si_3N_4 matrix composite processed at 1473 K in 1 atm N_2.[11] It should be noted, however, that the carbon/Si_3N_4 interface was at 1 atm $p(N_2)$ during the processing because the matrix has a porosity of 35%.[12] Since the $p(N_2)_{eq}$ for reaction (1) was less than 1 atm at the processing temperature (see Fig. 1), reaction (1) was effectively suppressed at the interface.

In Knudsen effusion, a dependence of vapor pressure on orifice size implies a kinetic barrier to equilibration.[9] In such a case, equilibrium pressure can be estimated by extrapolating the measured pressure at various orifice sizes to zero orifice size using the Whitman–Motzfeld equation.[13,14]

$$P_m = P_{eq} - (1/a + 1/W_A - 2)P_m W_B B/A \quad (6)$$

Here P_m is the measured pressure, P_{eq} is the equilibrium pressure, a is the vaporization coefficient, A is the cross-sectional

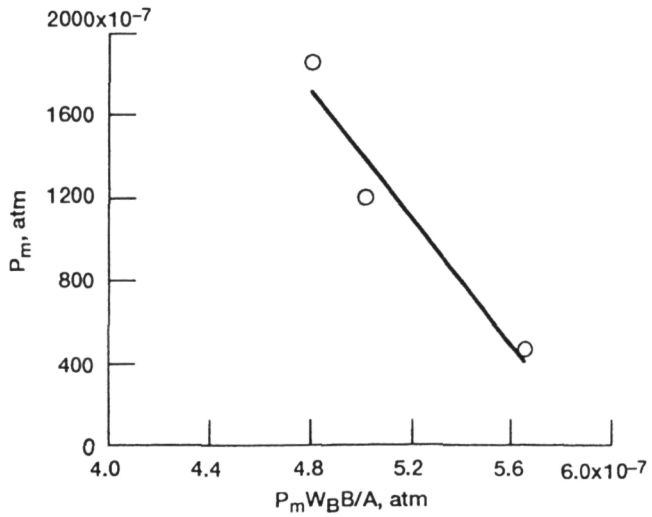

Fig. 6. Whitman–Motzfeldt extrapolation of $p(N_2)$ for the carbon/Si_3N_4 system at 1600 K.

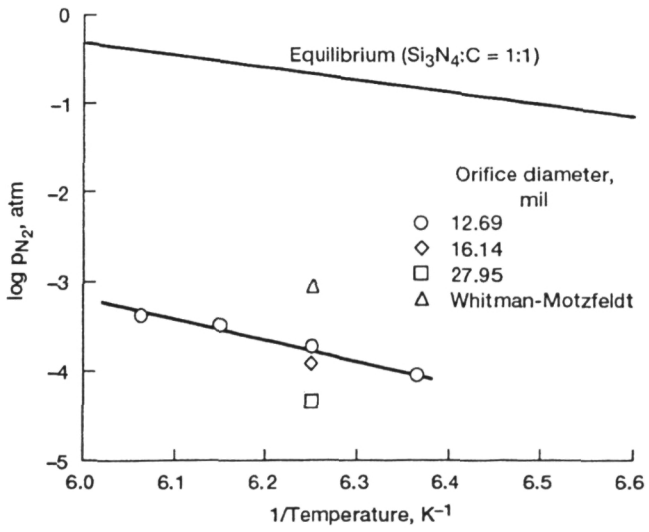

Fig. 7. Steady-state pressure of $N_2(g)$ for the carbon/Si_3N_4 system determined by the Knudsen effusion test. (Steady-state pressure is defined as the maximum pressure of $N_2(g)$ before it gradually decreases as shown in Fig. 4. The duration of steady state becomes longer with decreasing orifice diameter.)

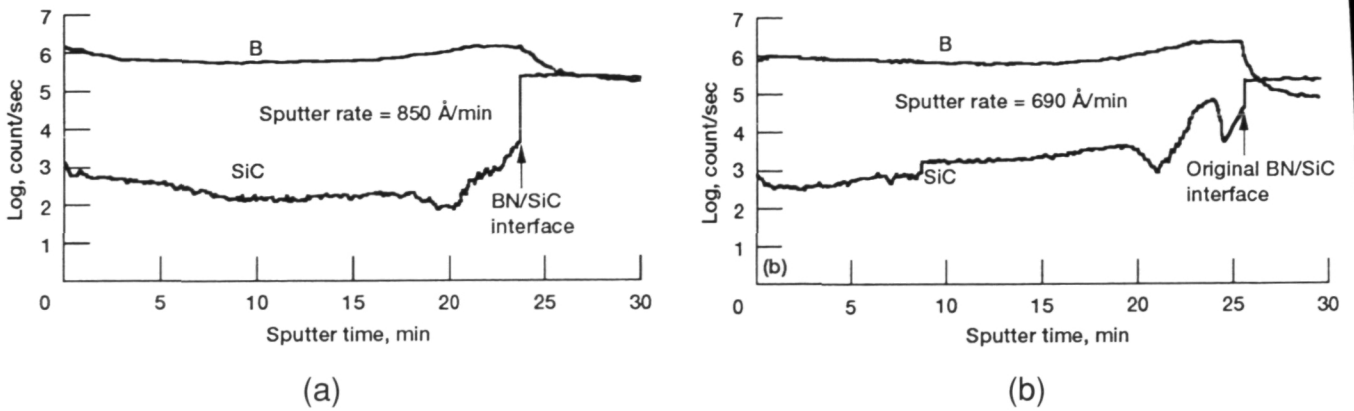

Fig. 8. SIMS analysis of the BN/SiC interface for a BN-coated SiC coupon. (a) As-coated. (b) After 50 h under vacuum at 1730 K.

area of the cell (0.316 cm^2), B is the orifice area ($8 \times 10^{-4} \sim 4 \times 10^{-3}$ cm^2), W_A is the Clausing factor of the cell, and W_B is the Clausing factor of the orifice (~1). The Clausing factor is the fraction of molecules escaping through an orifice or channel. Figure 6 is a plot of Whitman–Motzfeld extrapolation (Eq. (6)) to estimate $p(N_2)_{eq}$. Note the dependence of the measured $p(N_2)$ on the orifice size, confirming the existence of a kinetic reaction barrier. Figure 7 compares the estimated $p(N_2)_{eq}$ (triangle) with the calculated $p(N_2)_{eq}$. Even after the correction for the chemical reaction barrier, the estimated $p(N_2)_{eq}$ was about two orders of magnitude lower than the calculated $p(N_2)_{eq}$. This discrepancy is too large to be attributed to experimental errors. This indicates that there was another reaction barrier which was not considered in the Whitman–Motzfeld extrapolation. It appears that the SiC physical reaction barrier formed even before the reaction equilibrium was established, preventing the system from reaching equilibrium.

The heat of reaction can be calculated from the slope of log (K_p) vs $1/T$ using the Van't Hoff equation:

$$d \log [p(N_2)]^2/d\,(1/T) = -\Delta H/R \qquad (7)$$

Here ΔH is the heat of reaction, T is the absolute temperature, and R is a gas constant. The calculated heat of reaction was 895 kJ/mol, which was much higher than the equilibrium heat of reaction (530 kJ/mol). This also indicates that the measured $p(N_2)$ was not $p(N_2)_{eq}$.

If the reaction between carbon and Si_3N_4 continued as was thermodynamically predicted, either the coating would be depleted or a high $p(N_2)$ would be generated at the interface. However, the SiC physical reaction barrier prevented further reaction and the resultant development of high $p(N_2)$, limiting the predicted deleterious effects of the reaction. Furthermore, the shear property of carbon on Si_3N_4 is similar to that of carbon on SiC, so mechanical properties are not likely to be affected.

(2) BN/SiC System

No detectable weight loss was measured in the Knudsen effusion test for BN/SiC mixture, presumably because the weight loss due to the reactions between BN and SiC (reactions (3*a*)–(3*c*)) was below the resolution of the microbalance/Knudsen cell system.

Another possible route for the degradation of the BN/SiC interface is the solid-solution reaction between carbon and BN. BN is known to form a solid solution with graphite (BN_xC_{1-x}).[7,8] The optimum temperature for the formation of the solid solution is 1900°C, considerably higher than the anticipated application temperature of SiC/SiC composites (up to 1500°C). However, there is a driving force to form a solid solution, and over the long term the BN coating may dissolve in the matrix.

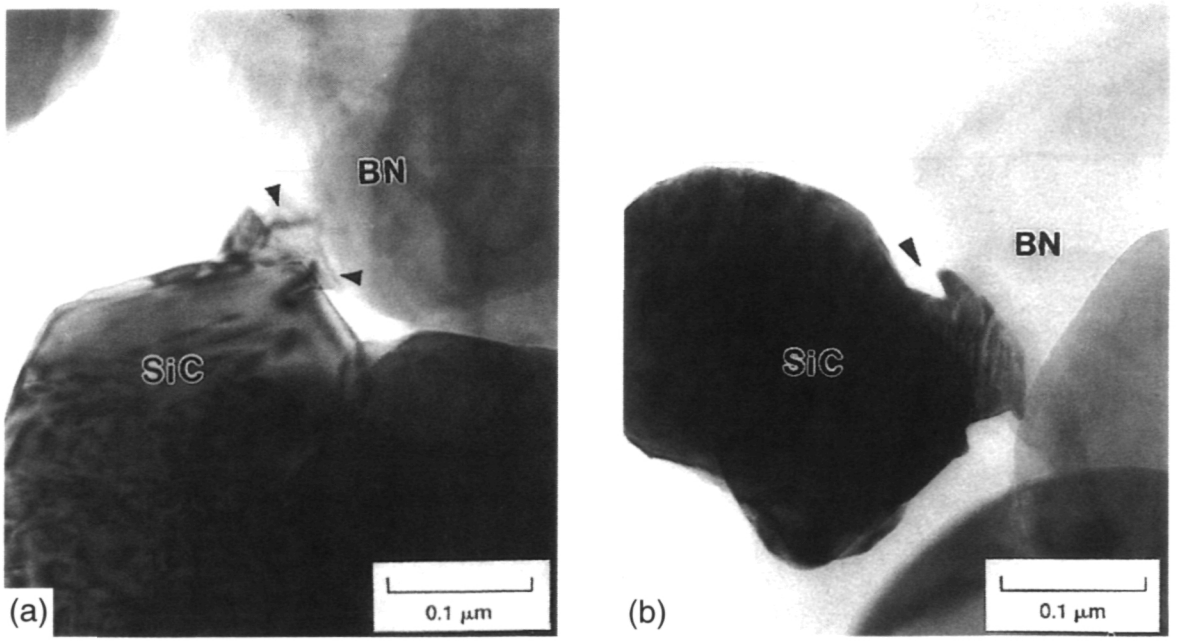

Fig. 9. TEM images of the reaction zone at the BN/SiC interface for a BN–SiC powder mixture after 170 h under vacuum at 1770 K. (a) and (b) are from different areas in the same batch.

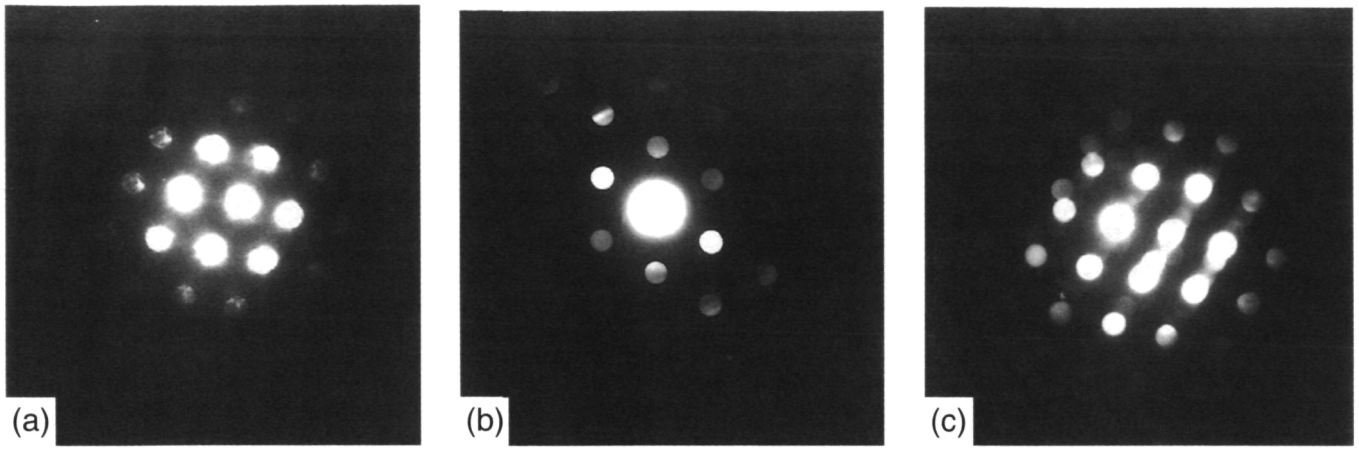

Fig. 10. Microdiffraction patterns at the BN/SiC interface for a BN–SiC powder mixture after 170 h under vacuum at 1770 K. (a) SiC. (b) BN. (c) Reaction zone.

Figures 8(a) and (b) are SIMS profiles[‡] of SiC and B in a BN-coated SiC coupon, as received and heat treated at 1730 K for 50 h, respectively. A peak in the SiC count was noticed in the heat-treated sample at the BN coating side of the interface. This feature was not observed in the as-received sample. Its presence suggests the existence of a reaction zone at the interface.

TEM analysis[§] of SiC/BN powder after the Knudsen effusion test at 1770 K for 170 h also showed a reaction zone at the BN/SiC interface as shown in Figs. 9(a) and (b). The fringe contours at the BN/SiC interface (arrow in Fig. 9(a)) indicate the existence of strain, presumably due to a reaction between BN and SiC. The reaction zone has grown further in Fig. 9(b) as shown by the arrows. Figures 10(a), (b), and (c) are microdiffraction patterns (μ-DP) for SiC, BN, and the reaction zone, respectively. Figure 10(c) shows only a limited match with the SiC diffraction pattern. There are clearly many features which are not from BN or SiC, suggesting the existence of a reaction zone. Further study is needed to identify the reaction product.

The reaction zone can potentially change the interface properties to limit the beneficial effects of the BN coating. In addition, in a long-term exposure, the BN layer may eventually be depleted, eliminating the beneficial effects of the coating.

V. Summary and Conclusions

Chemical reactions between the fiber coating and matrix materials in silicon-based ceramic matrix composites were investigated. Knudsen effusion was used to investigate gaseous and solid species, and coupon tests were used to simulate the coating/matrix interface and to investigate solid reaction products.

Carbon and Si_3N_4 reacted to form SiC and $N_2(g)$ as was thermodynamically predicted. Thermodynamic calculations predict that $p(N_2)$ reaches 1 atm at 1730 K, which can potentially disrupt the matrix. However, the reaction never reached equilibrium, for the SiC prevented further reaction and thus reduced $p(N_2)$ by three orders of magnitude. As a result, the predicted deleterious effect of the reaction on the composite is likely to be limited.

BN and SiC did not generate any significant amount of gaseous species as was thermodynamically predicted. However, there were indications of a reaction zone at the interface by SIMS analysis of the BN-coated SiC coupon and TEM analysis of reacted powders in the Knudsen cell. The reaction can potentially change the interface properties to limit the beneficial effects of the BN coating. In a long-term exposure, the BN layer may eventually be depleted.

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[‡]Analysis performed at Perkin Elmer, Eden Prairie, MN.
[§]Analysis performed at R. J. Lee Group, Inc., Berkeley, CA.